EXCERPT: Diffusion Sampler Evaluation of Chlorinated VOCs in Groundwater
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User’s Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells

Part 2: Field Tests

By Don A. Vroblesky, *editor*

U.S. Geological Survey

Water-Resources Investigations Report 01–4061

Prepared in cooperation with the

U.S. AIR FORCE

U.S. NAVAL FACILITIES ENGINEERING COMMAND

U.S. ENVIRONMENTAL PROTECTION AGENCY

FEDERAL REMEDIATION TECHNOLOGIES ROUNDTABLE

DEFENSE LOGISTICS AGENCY

U.S. ARMY CORPS OF ENGINEERS and

INTERSTATE TECHNOLOGY REGULATORY COOPERATION WORK GROUP

Columbia, South Carolina
2001

Diffusion Sampler Evaluation of Chlorinated VOCs in Groundwater

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ABSTRACT: Groundwater sample collection using diffusion samplers represents a relatively new technology that utilizes passive sampling methods for monitoring volatile organic compounds (VOCs) in groundwater. The potential benefits and cost savings of diffusion sampler use as an instrument for long-term monitoring are significant, as no purge waters are generated, and labor requirements for sampler installation and retrieval are minimal. The efficacy of diffusion samplers for evaluating chlorinated VOCs in groundwater was assessed. Using two types of diffusion samplers, groundwater samples were collected at discrete depths to assess vertical contamination profiles. Groundwater samples also were collected following low-flow/minimal drawdown purging and conventional purging techniques. Results obtained using the various sampling techniques suggest that the diffusion samplers provide comparable accuracy with and can be significantly less expensive than traditional sampling techniques.

INTRODUCTION

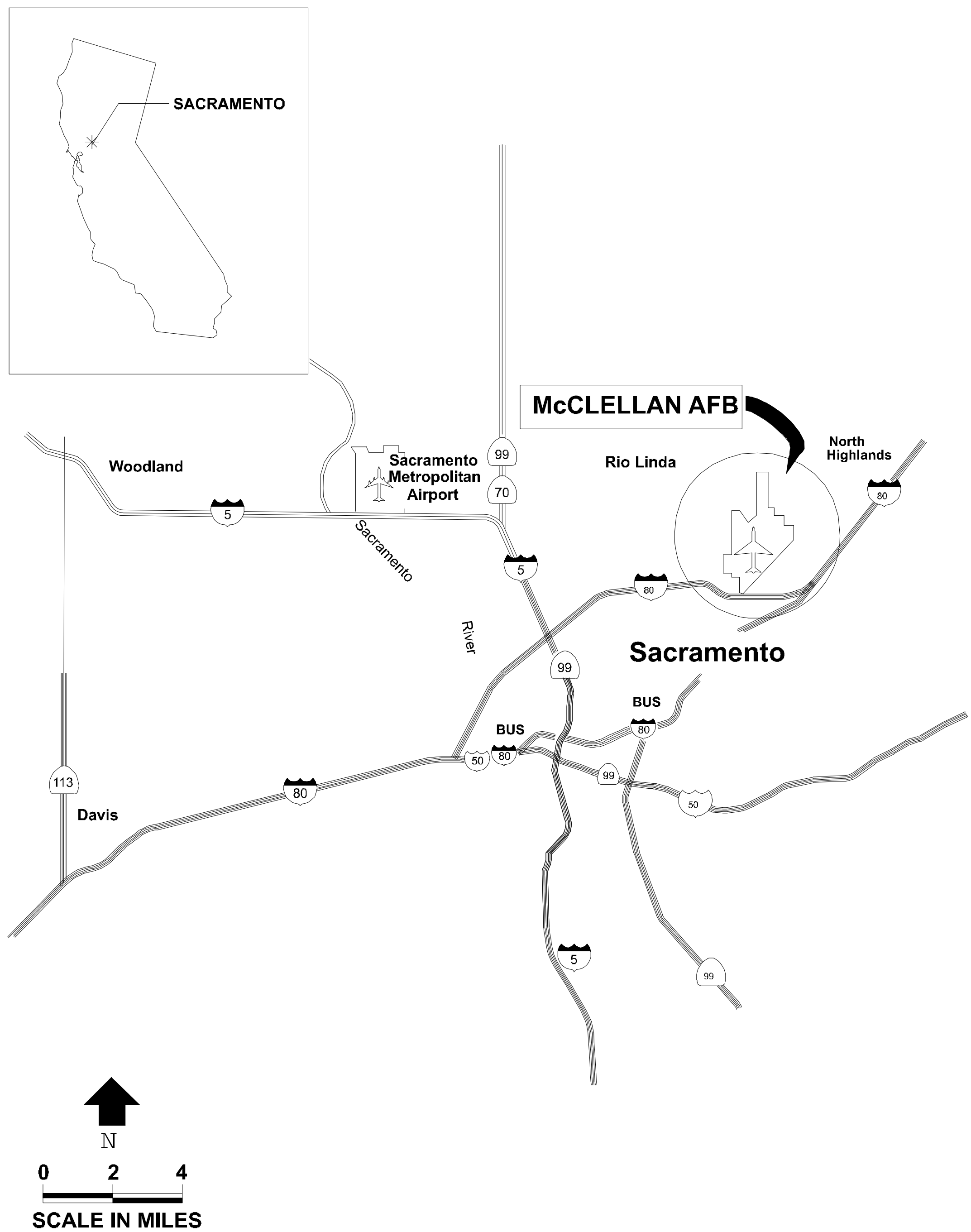
Parsons Engineering Science, Inc. (Parsons ES) was retained by the US Air Force Center for Environmental Excellence, Technology Transfer Division (AFCEE/ERT) to perform an evaluation of passive groundwater diffusion sampling technology. The diffusion sampler evaluation is part of the AFCEE/ERT Remedial Process Optimization (RPO) demonstration project being performed at six Air Force bases (AFBs) nationwide. One of these bases, McClellan AFB, California (figure 1), was selected as the site for this evaluation. A field study was performed in August 1999 at a site on McClellan AFB where deep groundwater, more than 30 meters below ground surface, is contaminated with various chlorinated VOCs as a result of solvent disposal into burn pits during the 1940s through 1970s.

The objective of the diffusion sampler evaluation was to evaluate the efficacy of this groundwater sampling method relative to standard sampling methods. Field sampling was conducted using two types of diffusion samplers to collect groundwater samples from varying depths at selected monitoring wells. The diffusion samplers evaluated included the commercially available DMLS™ sampler (obtained from Johnson Screens, New Brighton, Minnesota in August 1999), and a sampler currently being developed and used by the US Geological Survey (USGS). The standard sampling methods used for comparison to the diffusion sampling results were:

1. Groundwater sampling following conventional purging of at least 3 casing-volumes of water and stabilization of water quality parameters (i.e., conventional sampling); and
2. Sampling following low-flow/minimal drawdown purging (i.e., micropurging). The groundwater samples were analyzed for total VOCs using US Environmental Protection Agency (USEPA) Method SW8260B/5030 (USEPA, 1994).

FIGURE 1

SITE LOCATION



MATERIALS AND METHODS

Diffusion sampling is a relatively new technology designed to use passive sampling techniques that eliminate the need for well purging. A diffusive-membrane capsule is filled with deionized distilled water, sealed, mounted in a suspension device, and lowered to a specified depth in a monitoring well. Over time (no less than 72 hours), VOCs in the groundwater diffuse across the capsule membrane, and contaminant concentrations in the water inside the sampler attain equilibrium with the ambient groundwater. The sampler is subsequently removed from the well, and the water within the diffusion sampler is transferred to a sample container and submitted for analysis. The diffusive membranes evaluated in this study are rated for VOCs only. These membranes are not appropriate for monitoring larger or more electrically charged molecules.

Once a diffusion sampler is placed in a well, it remains undisturbed until equilibrium is achieved between the water in the well casing and the water in the diffusion sampler. Depending on the hydrogeologic characteristics of the aquifer, the diffusion samplers can reach equilibrium within 3 to 4 days (Vroblesky and Campbell, 1999); however for this evaluation, a minimum 14-day equilibrium period was used. Groundwater samples collected using the diffusion samplers are thought to be representative of water present within the well during the previous 24 to 72 hours.

USGS Sampler.—The standard USGS diffusion sampler, shown in figure 2, consists of water-filled, low-density polyethylene tubing, which acts as a semi-permeable membrane. The USGS sampler typically is constructed of a 45-centimeter (cm)-long section of 5.08-cm-diameter, 4-mil polyethylene tubing that is heat-sealed on both ends. The sampler holds approximately 300 milliliters (mL) of deionized distilled water. A longer 7.62-cm-diameter sampler that holds approximately 500 mL of water also is available if larger sample volumes are required. The sampler is placed in "flex-guard" polyethylene mesh tubing for abrasion protection, attached to a weighted rope, and lowered to a predetermined depth within the screened interval of a well. The rope is weighted to ensure that the sampling devices are positioned at the correct depth and that they do not float upward through the water column.

FIGURE 2

USGS DIFFUSION SAMPLER

Assembled USGS sampler being lowered into monitoring well

USGS sampler prior to sample collection

For this evaluation, multiple USGS samplers were placed end-to-end in three test monitoring wells to develop vertical contamination profiles. Upon recovery, the samplers were cut open, and water samples were transferred into 40-mL volatile organics analysis (VOA) vials. The samples were preserved and submitted for analysis.

DMLSTM Sampler.—The DMLS™ sampler, shown in figure 3, uses dialysis cells as passive collection devices. The dialysis cells are composed of a polypropylene cylinder that holds 38 mL of deionized distilled water. The cells have 0.2-micrometer cellulose acetate filters attached to each end of the cell that serve as the permeable membranes. The cells are mounted in cylindrical holes pre-drilled through a 152-cm-long polyvinyl chloride (PVC) rod, and are separated by viton spacers, or well seals, that fit the inner diameter of the well. The PVC rod can accommodate as many as 12 sampling cells (pre-drilled cylindrical hole spacing is 12.7 cm), and a string of up to 5 rods can be connected together for sampling over long screened well intervals.

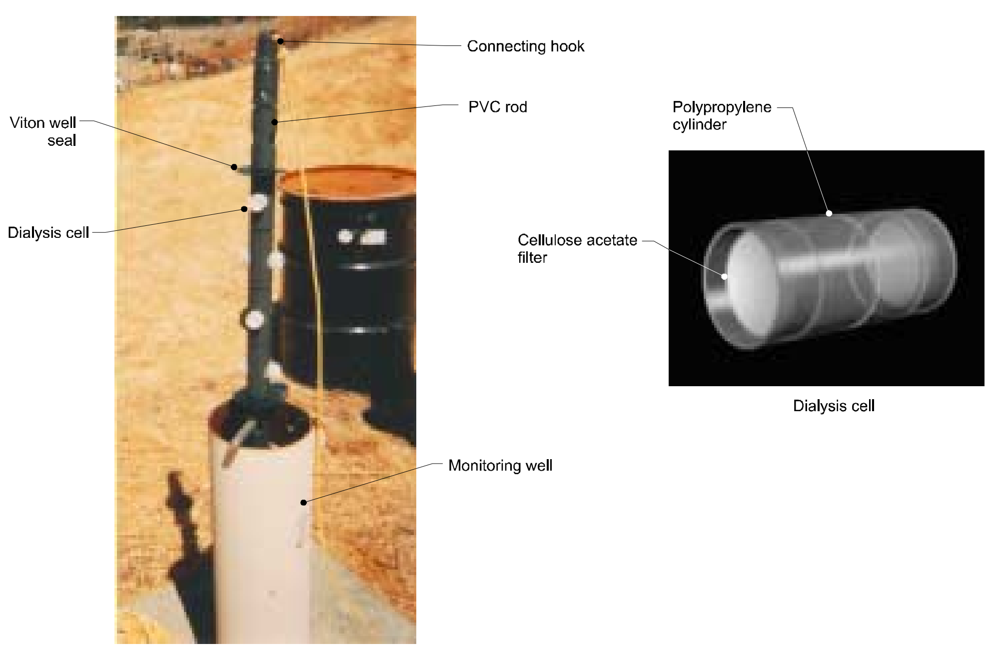
Once loaded with the prepared dialysis cells, the PVC rods are lowered into a well to the desired depth within the screened interval, and are secured with a rope to the top of the well casing. A stainless steel weight is attached to the bottom of the deepest PVC rod to ensure that the samplers are positioned at the correct depth in the well, and that the PVC rods do not float through the water column.

Upon retrieval of the PVC rods, the dialysis cells are removed from the PVC rod, emptied into a decontaminated container for compositing, and then transferred to 40-mL VOA containers. The samples are preserved and sent to a laboratory for analysis.

Conventional Sampling.—Groundwater sampling using conventional well purging involves removing a large volume of water (3 to 5 well casing-volumes) from the well over a short time. The objective of conventional purging is to remove all water present within the well casing, as well as groundwater present in the surrounding well filter pack. Theoretically, by removing this water quickly, the “stagnant” water that resided in the well and filter

FIGURE 3

DMLS™ DIFFUSION SAMPLER



Assembled DMLS™ sampler prior to being lowered into monitoring well

Dialysis cell

pack will be replaced with “fresh” groundwater from the surrounding formation with minimal mixing. The “fresh” groundwater that is then sampled is considered to be representative of the local groundwater. Rapid drawdown of the water level in a well is not uncommon, and often wells are purged dry using this method. Conventional purging is frequently performed using a bailer or a high-flow submersible pump (e.g., Grundfos Redi-Flo2 pump).

Micropurging. —The objective of micropurging is to remove a small volume of water at a low flow rate from a small portion of the screened interval of a well without mixing water among vertical zones. Ideally, by placing the inflow port of a pump at a prescribed depth within the screened interval of a well, and by withdrawing water at a slow rate, groundwater will be drawn from the aquifer into the well only in the immediate vicinity of the pump. This discrete-depth sampling allows for vertical definition of contamination in the aquifer. The pumping rate is adjusted to minimize drawdown. Because micropurging relies on a pumping rate that does not exceed the natural groundwater recharge rate, the water elevation in the well must be monitored to ensure that drawdown does not occur.

Field Activities.—Three monitoring wells were selected for use in this evaluation. In each of the wells, a maximum of three depth intervals spaced equally across the well screen were monitored using the different sampling methods. Using the two types of diffusion samplers as designed, it was necessary to perform the diffusion sampling consecutively, as samples from the two types of diffusion samplers could not be collected concurrently from the same interval within a well. To evaluate the potential changes in groundwater concentrations over the sampling periods (approximately 14 days between diffusion sampler collection events), conventional groundwater sampling was performed following completion of each diffusion sampling event. Significant differences in groundwater chemistry measured between the two sampling events could be normalized using the two sets of conventional groundwater data.

RESULTS AND DISCUSSION

Of the 67 analytes included in the SW8260B analysis, 17 were reported to have detectable concentrations in at least one of the samples submitted for analysis. For the purposes of comparing the analytical accuracy or comparability using the different sampling methods, only those analytes that were detected in at least 10 samples were considered in this study. These analytes include trichloroethene (TCE), *trans*-1,2-dichloroethene (DCE), *cis*-1,2-DCE, 1,1-DCE, 1,1-dichloroethane (DCA), 1,2-DCA, and 1,1,2-trichloroethane (TCA). A summary of analytical results for these analytes is presented in table 1.

The different methods of sample collection were evaluated using the following criteria: accuracy or comparability of data, other method-specific criteria, and cost. These criteria are described in the following sections.

Accuracy/Comparability of Data.—The analysis-of-variance (ANOVA) test was used to compare analytical data collected using the different sampling techniques. The limited number of samples available (as few as 3 per sampling method) precluded the use of linear statistical models in a quantitative manner. Therefore, the ANOVA was used in a qualitative manner to provide a "weight-of-evidence" support for data accuracy and similarity.

The ANOVA test returns a “p-value” between zero and one, indicating a “pass” or “fail” condition. A p-value of 0.05 or greater represents a pass, indicating that the distributions are similar at the 95-percent confidence level.

ANOVA is a parametric test, and it is common practice to verify that the data fit a parametric distribution prior to applying the tests. However, due to the limited number of samples in the data set, normality tests were not performed on the data sets before performing the ANOVA.

In instances where a nondetectable concentration of an analyte was reported for a sample, a value of zero was assigned for the purposes of the ANOVA testing only. For the conventional purging, each of the three depth intervals evaluated was assigned the same analytical value reported for the one sample collected from that well.

Table 1. Analytical results for samples

[µg/L, migrograms per liter]

Well ID	First Mobilization			Second Mobilization	
	USGS	Micropurge	Conventional	DMLS™	Conventional
TCE (µg/L)					
MW11	8 to 23	24	29	8 to 10	21
MW241	3.8 to 40	27 to 33	41	27 to 33	32
MW242	3.4 to 6	2.8 to 3.5	4	3.3 to 5.3	3.1
***trans*-1,2-DCE (µg/L)**					
MW11	ND	ND	ND	ND	ND
MW241	ND to 1.2	0.90 to 0.98	1	0.77 to 1.4	0.99
MW242	ND	ND	ND	ND	ND
***cis*-1,2-DCE (µg/L)**					
MW11	0.95 to 2.3	3.4	3.8	1.1 to 1.4	3.3
MW241	0.63 to 9.2	6.5 to 7.2	7.2	6 to 11	6.8
MW242	ND	ND	ND	ND	ND
1,1-DCE (µg/L)					
MW11	34 to 89	170	220	58 to 77	170
MW241	2.1 to 22	15 to 19	23	19 to 21	18
MW242	4.4 to 9	3.8 to 6.3	5.4	5.2 to 10	3.1
1,1-DCA (µg/L)					
MW11	0.66 to 1.6	1.6	1.7	0.54 to 0.69	1.5
MW241	0.36 to 4.4	3.5 to 3.6	3.6	2.9 to 4.3	3.4
MW242	ND	ND	ND	ND to 0.22	ND
1,1,2-TCA (µg/L)					
MW11	0.58 to 1.6	1.3	1.6	0.47 to 0.68	1.5
MW241	0.32	0.23 to 0.28	0.32	0.22 to 0.27	0.27
MW242	ND	ND	ND	ND	ND
1,2-DCA (µg/L)					
MW11	0.95 to 2.2	2.2	2	0.74 to 0.83	1.9
MW241	1.8 to 16	14 to 16	15	12 to 15	15
MW242	0.43 to 1.6	0.98 to 3.5	5.3	0.78 to 1.4	3.6

Notes:

- “8 to 23” – Range of concentrations measured over sampled depth intervals.
- ND – Not detected.
- Data validation qualifiers did not affect the usability of the data for this evaluation and are therefore not included in table 1.

As presented in table 2, in all instances the p-values calculated for the populations of results for the different sampling methods exceeded 0.05. These ANOVA results indicate that there are no statistically significant differences among analytical results obtained using the four groundwater sampling techniques. Given that the evaluated diffusion samplers provide comparable accuracy with traditional sampling techniques, other criteria must be considered in evaluating the suitability of one sampling technique over another.

Table 2. ANOVA results

Analyte	p-value
1,1,2-TCA	0.74
1,1-DCA	0.99
1,1-DCE	0.47
1,2-DCA	0.88
cis-1,2-DCE	0.96
TCE	0.59
trans-1,2-DCE	0.99

Other Method-Specific Criteria.—Additional qualitative and semi-quantitative criteria were considered in this evaluation and are sumarized in table 3.

Table 3. Summary of other method-specific criteria results

Criteria	USGS	DMLS™	Micropurge	Conventional
Ease of use	Excellent	Fair	Poor	Fair
Labor hours required per sample	0.66	1	2.75	3.66
Generation of IDW (liters)	< 1	< 1	100	500
Cost to provide dedicated equipment in each well	Low	High	Low	High
Decontamination required if dedicated equipment is not used	Minimal	High	Moderate	Moderate
Immediacy of sample availability	Slow	Slow	Rapid	Rapid
Can analytes other than VOCs be monitored?	No	No	Yes	Yes
Can vertical distribution of contaminants be evaluated?	Possible	Possible	Partial	No
Suitable for natural attenuation monitoring?	No	No	Yes	Partial

Supplemental to the criteria shown in table 3, concerns specific to the USGS and DMLS™ samplers were noted. Being placed in a well for potentially long periods, these samplers are susceptible to the effects of fluctuating groundwater elevations. If groundwater elevations decrease such that a portion of the diffusion sampler is exposed to air, the potential exists for volatilization of VOCs, which would compromise the samples collected from these devices.

A second concern was identified with the DMLS™ sampling device in that the sample volume of each dialysis cell is only 38 mL. When collecting samples for VOC analysis, the typical sample container is a 40 mL VOA, which will require more than one dialysis cell to fill.

As shown in table 3, many benefits can be realized through the use of diffusion samplers, however these devices also present limitations which may preclude their use in certain groundwater sampling applications.

Cost.—Cost estimates per sample for each of the four sampling methods evaluated are presented in table 4. The following expenses were considered in the development of a cost analysis for each different sampling method: labor, equipment, and disposal or management of investigation-derived waste (IDW). Some of the costs involved in these activities are one-time expenses that are not incurred each time a sample is collected (e.g., PVC rods for use with the DMLS™ samplers and stainless steel weights). Furthermore, labor and material costs can vary depending on the scope of the sampling event (e.g., it is less expensive on a unit-cost basis to collect 100 samples than to collect 5 samples). However, to present the most accurate estimate of costs associated with this evaluation, only the costs incurred during this field study were considered in the cost analysis. Labor costs were based on actual hours expended as documented in the field notes and the burdened labor rate for a typical field scientist. Equipment costs were taken directly from invoices (when available) or were estimated from vendor quotes. Costs associated with disposal or management of IDW can vary widely depending on the approach used. For this analysis, the only costs considered in the management of IDW are those dealing with containerizing the waste.

Table 4. Cost summary

Sampling technique	Cost per sample
USGS	$65
DMLS™	$555
Micropurge	$308
Conventional	$444

As noted, these costs are approximated based on the limited scope of this investigation. If these sampling technologies were applied to large-scale monitoring programs, a reduction in the per-sample cost would probably be realized due in part to reusable equipment that is associated with some of the sampling methods.

As shown in table 4, the cost per sample using the USGS diffusion sampler was substantially less than using any other methods. Conversely, the DMLS™ sampler per sample cost was substantially more that any other method.

CONCLUSIONS

The Air Force groundwater diffusion sampler evaluation indicates that diffusive sampling technology can be a cost-effective and accurate method for environmental groundwater monitoring of VOCs. However, use of diffusion samplers may not be appropriate for all applications. Of the diffusion sampling technologies evaluated, the USGS sampler is the recommended device based on the evaluation criteria presented herein. Additional comparisons between the different sampling technologies should be performed to develop a more robust data set upon which to base analytical result comparisons. Particularly, varying hydrogeologic settings (e.g., low-permeability to high-permeability aquifers) and increasing the number of wells in the evaluation would allow for more thorough evaluation of the comparability of the analytical data.

If natural attenuation monitoring is required, a combination of sampling techniques should be considered. For instance, annual monitoring of natural attenuation parameters can be performed using a traditional sampling method, while quarterly monitoring of VOCs can be accomplished using diffusion sampling technology.

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